ELSEVIER

Catalysis Today 38 (1997) 151–156

CATALYSIS TODAY

Experimental and theoretical studies of NO decomposition and reduction over metal-exchanged ZSM-5

Alexis T. Bell*

Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California, Berkeley, CA 94720, USA

Abstract

Metal-exchanged zeolites and, in particular, ZSM-5 are candidate catalysts for NO decomposition and reduction. Results of experimental and theoretical studies are presented which focus on understanding the nature of the catalytically active sites and the elementary processes involved in the decomposition of NO over Cu-ZSM-5 and the reduction of NO over Co-ZSM-5.

Keywords: Decomposition; Nitric oxide; Zeolite; Metal exchange

1. Introduction

Stationary sources such as power plants contribute roughly half of all of the NO emitted into the atmosphere from combustion [1]. Currently much of the NO emissions from these stationary sources is controlled by selective catalytic reduction (SCR). In this process, NO is reduced in the presence of O_2 by NH_3 over titania-supported vanadia. While this technology is effective, the use of ammonia as the reductant is undesirable for a number of reasons. First, large quantities of ammonia must be stored either as liquid ammonia or ammonium hydroxide, raising the risk of release of a toxic compound. Second, the introduction of ammonia to the SCR process must be carefully controlled to avoid ammonia slippage into the effluent gases leaving the convertor. Third, ammonia in the reactor effluent can react with water and sulfur trioxide to produce ammonium sulfate which can deposit onto the surfaces of the heat exchanger thereby causing a reduction in heat transfer efficiency. For all of these reasons there is a strong interest in finding alternative means for controlling NO emissions from stationary sources.

Recent studies have shown that metal-exchanged zeolites can catalyze the decomposition of NO to N_2 and O_2, and the selective reduction of NO by CH_4 (e.g., Ref. [2] and references cited therein). Copper-exchanged ZSM-5 is particularly attractive for the first of these reactions and Co-exchanged ZSM-5 is one of the most active catalysts for the second reaction. We have undertaken both experimental and theoretical studies with the aim of understanding the structure of Cu- and Co-exchanged ZSM-5, and the manner in which these catalysts facilitate the decomposition and reduction of NO. An overview of our efforts is presented below.

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*Corresponding author. Tel.: (1-510) 642-1536; Fax: (1-510) 642-4778.

PII S0920-5861(97)00059-X

2. Cu-ZSM-5

EPR studies demonstrate that immediately after exchange all of the copper in Cu-ZSM-5 is present as Cu^{2+}, presumably as hydrated $Cu^{2+}(OH)^-$ [3]. Heating freshly prepared Cu-ZSM-5 in flowing He or in vacuum results in the autoreduction of Cu^{2+} to Cu^+ [3–5]. This transformation was originally inferred from EPR [3–9] and photoluminescence [10,11] observations and has now been confirmed by XANES [6,12,13]. We have very recently shown by means of ^{65}Cu NMR and ^{27}Al–^{65}Cu SEDOR NMR experiments that all of the Cu^+ species formed by autoreduction are associated with Al cation-exchange sites, and that the average Cu-Al distance is 2.3 ± 0.2 Å [14]. We have also proposed that the autoreduction process proceeds via the reaction $2Cu^{2+}(OH)^- = Cu^+ + Cu^{2+}O^- + H_2O$, since all of the copper can be transformed back to Cu^{2+} by exposing an autoreduced sample of Cu-ZSM-5 to water vapor [3]. Density functional theory (DFT) calculations demonstrate that both Cu^+ and $Cu^{2+}O^-$ are strongly bidentate coordinated with oxygen atoms bonded to Al in the zeolite framework, as shown in Figs. 1 and 2 [15]. The distance of Cu^+ from Al in a T12 site is 2.4 Å, in very close agreement with what is found experimentally. The DFT calculations also show that both Cu^+ and $Cu^{2+}O^-$ have negligible net spin and hence should be EPR silent.

Infrared studies show that NO absorption occurs on both Cu^+ and $Cu^{2+}O^-$ [16]. The band observed at $1811\ cm^{-1}$ is attributed to $Cu^+(NO)$ and a pair of bands at 1824 and $1733\ cm^{-1}$ are attributed to $Cu^+(NO)_2$. A band seen at $1906\ cm^{-1}$ is assigned to $Cu^{2+}(O^-)(NO)$. Additional bands are observed below $1600\ cm^{-1}$ have been attributed to nitrito and nitrato species. DFT calculations reveal that while NO adsorbed as $Cu^+(NO)$ and $Cu^{2+}(O^-)(NO)$ is strongly bound, NO in $Cu^+(NO)_2$ is not [17]. The heats of NO adsorption for the first two species are 43.3 kcal/mol and 53.7 kcal/mol, respectively, whereas the heat of adsorption for the third is 54.5 kcal/mol. These findings are consistent with experimental observation.

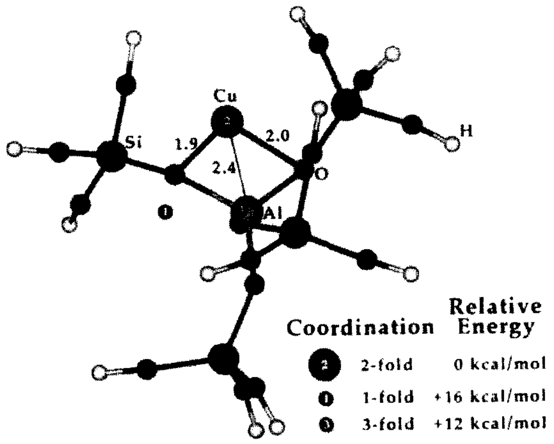


Fig. 1. The structure and bonding of Cu^+ in ZSM-5.

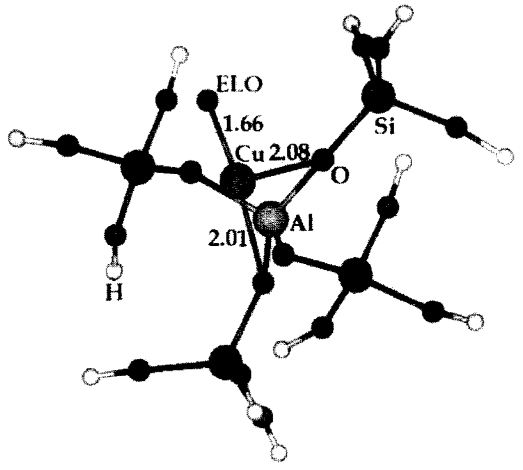


Fig. 2. The structure and bonding of $Cu^{2+}O^-$ in ZSM-5.

The nature of the species involved in NO decomposition over Cu-ZSM-5 is revealed by infrared spectroscopy. NO decomposition over Cu-ZSM-5 initiates above 573 K and reaches a maximum at about 523 K. In this temperature range, in situ infrared spectra show weak bands for only two species, $Cu^+(NO)$ and $Cu^{2+}(O^-)(NO)$ [16]. Several authors [11,18–23] have proposed that Cu^+ sites are essential for NO decomposition, and a correlation has been reported between the concentration of Cu^+ sites and the activity of Cu-ZSM-5 for NO decomposition [11]. While it has also been proposed [2,24] that only Cu^{2+} sites are required for NO decomposition, the experimental evidence for this interpretation is not compelling.

To assess whether or not NO decomposition could occur over isolated Cu sites and the extent to which Cu^+ and $Cu^{2+}O^-$ are involved, we have carried out a theoretical analysis of the Gibbs free energies of

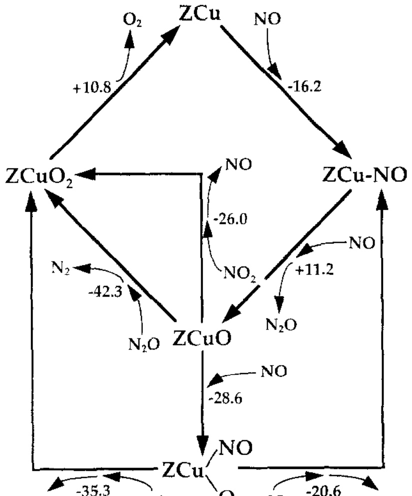


Fig. 3. Proposed mechanism for NO decomposition over Cu-ZSM-5.

reaction for a sequence of steps comprising a mechanism for NO decomposition [17]. Fig. 3 illustrates a reaction mechanism based on choosing those elementary processes for which the change in the Gibbs free energy is most favorable. The numbers appearing in this figure give the change in the standard-state Gibbs free energy for each elementary step evaluated at 500°C. Based on this analysis it is clear that NO decomposition could occur via a reaction sequence involving only Cu^+ and $Cu^{2+}O^-$ as the catalytically active sites.

The reaction mechanism shown in Fig. 3 is consistent with a number of experimental observation. As noted earlier, in situ infrared spectroscopy shows only two forms of adsorbed NO at temperatures in the range of 400–500°C where the rate of NO decomposition is significant. While it has been suggested that N_2O could form via the decomposition of $Cu^+(NO)_2$, our calculations show that this species is not stable in the temperature range of interest [17]. Thus it is far more likely that N_2O is formed via the reaction of NO with $Cu^+(NO)$. The decomposition of NO is known to be inhibited by O_2 [9]. Fig. 3 suggests that with increasing O_2 partial pressure, the rate of NO decomposition is inhibited by blocking the release of Cu^+ sites. H_2O is also known to inhibit NO decomposition over Cu-ZSM-5 [2]. While the interactions of H_2O with Cu-ZSM-5 are not shown in Fig. 3, we have calculated that the change in the standard-state Gibbs free energy for the reaction $Cu^+ + Cu^{2+}O^- + H_2O = 2\,Cu^+(OH)^-$ to be -18 kcal/mol at 500°C [15]. From this we deduce that H_2O could inhibit the decomposition of NO by reducing the concentrations of Cu^+ and Cu^{2+}, both of which are envisioned to be essential species for NO decomposition.

3. Co-ZSM-5

Studies by different investigators have shown that Co-ZSM-5 is not very active for the reduction of NO by CH_4 in the absence of O_2 [25–30]. Introduction of O_2 into the feed stream greatly enhances the reduction of NO to N_2. This effect has been ascribed to the oxidation of NO to NO_2, which is then strongly adsorbed on the catalyst where it is attacked by CH_4. Direct observation of the reaction of NO_2 with methane has recently been obtained from infrared studies [31,32]. Figs. 4 and 5 show spectra taken

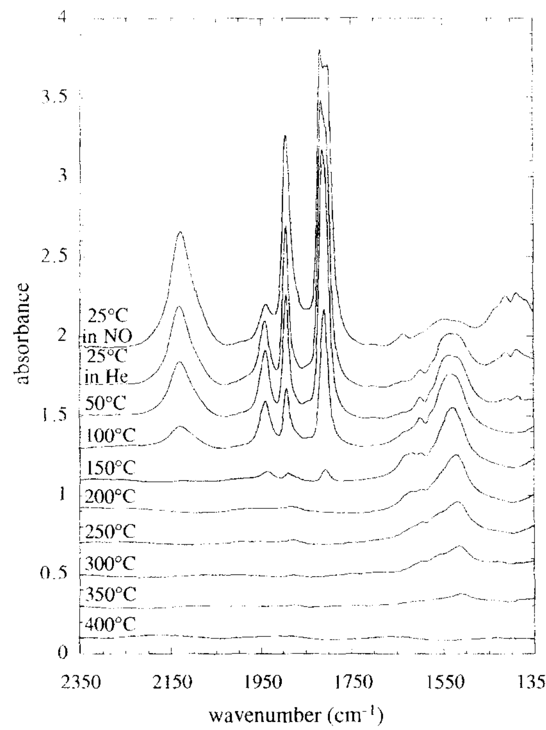


Fig. 4. Infrared spectra taken during temperature programmed desorption of NO in He.

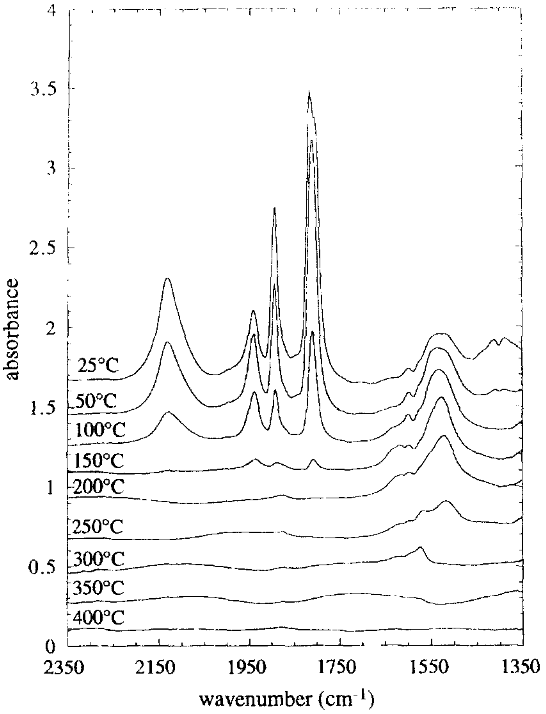
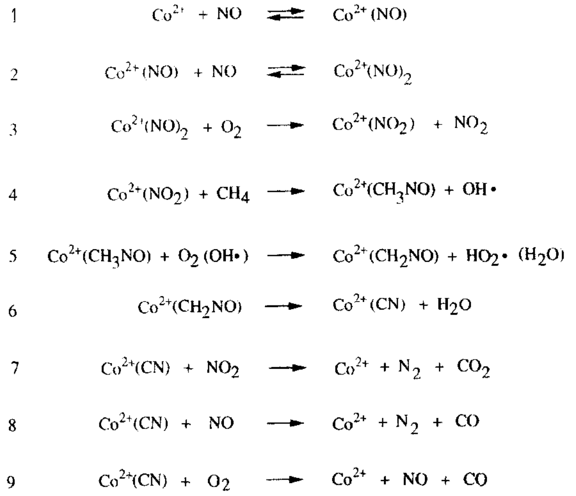


Fig. 5. Infrared spectra taken during temperature programmed desorption of NO in CH_4.



$$1 \quad Co^{2+} + NO \rightleftharpoons Co^{2+}(NO)$$

$$2 \quad Co^{2+}(NO) + NO \rightleftharpoons Co^{2+}(NO)_2$$

$$3 \quad Co^{2+}(NO)_2 + O_2 \rightarrow Co^{2+}(NO_2) + NO_2$$

$$4 \quad Co^{2+}(NO_2) + CH_4 \rightarrow Co^{2+}(CH_3NO) + OH\bullet$$

$$5 \quad Co^{2+}(CH_3NO) + O_2\,(OH\bullet) \rightarrow Co^{2+}(CH_2NO) + HO_2\bullet\ (H_2O)$$

$$6 \quad Co^{2+}(CH_2NO) \rightarrow Co^{2+}(CN) + H_2O$$

$$7 \quad Co^{2+}(CN) + NO_2 \rightarrow Co^{2+} + N_2 + CO_2$$

$$8 \quad Co^{2+}(CN) + NO \rightarrow Co^{2+} + N_2 + CO$$

$$9 \quad Co^{2+}(CN) + O_2 \rightarrow Co^{2+} + NO + CO$$

Fig. 6. Proposed mechanism for NO reduction by CH_4 over Cu-ZSM-5.

during the temperature programmed desorption of NO in either flowing He or CH_4 [32]. Below 250°C both sets of spectra are identical. Bands are seen at 2132 cm^{-1} due to $H^+(NO_2)$, 1941 cm^{-1} due to $Co^{2+}(OH^-)(NO)$, 1894 and 1815 cm^{-1} due to $Co^{2+}(OH^-)(NO)_2$, 1633 cm^{-1} due to nitrate species, and 1560–1530 cm^{-1} due to nitrito species. Above 250°C the intensity of the nitrito band is significantly reduced by reaction with CH_4.

During steady-state reaction of NO with CH_4, two additional bands are observed at 2270 and 2173 cm^{-1}. These features have been assigned to $Al^{3+}(NCO)$ and $Co^{2+}(OH^-)(CN)$, respectively [32,33]. To assess whether these species might be reaction intermediates, experiments were carried out in which the isocyanate and cyanide species were prepared and then allowed to react with NO, O_2, or NO_2 at 450°C and the rate of species disappearance was compared with that observed in flowing He. Significant acceleration in the rate of band attenuation was observed only in the case of the cyanide species, with the rate of consumption of cyanide species increasing in the order $NO_2 \gg NO \approx O_2 > He$. In a complimentary set of experiments the products formed via reaction of NO, O_2 or NO_2 with cyanide species was followed by mass spectrometry [33]. The dynamics of cyanide consumption determined by this means were virtually identical to those determined from infrared observations. Both N_2 and CO_2 were observed upon reaction of cyanide species with NO_2 and O_2, and the stoichiometric ratios in which these products were formed are consistent with assignment of the band at 2173 cm^{-1} to CN.

Based on the evidence presented above we propose the mechanism for NO reduction by CH_4 presented in Fig. 6. This scheme is based upon an amalgamation of elementary steps previously suggested in the literature [28–31,34–36] and those deduced from the experiments presented here. The sequence begins with the adsorption of NO adsorption to form both mono- and dinitrosyl species (Reactions 1 and 2). The later species undergo oxidation in O_2 (Reaction 3) to form adsorbed and gas-phase NO_2. The reaction of CH_4 with adsorbed NO_2 (Reaction 4) is assumed to form an hydroxyl radical and adsorbed CH_3NO. Weiner and Bergman [37] have reported the formation of CH_3NO and other nitrosoalkanes by migratory insertion of coordinated NO into Co–C bonds of cobalt alkyl species. Subsequent reaction of adsorbed nitrosomethane with either OH radicals or O_2 (Reaction

5) followed by the elimination of water (Reaction 6) leads to the formation of adsorbed CN species. The nitrile species are hypothesized to react with NO_2 to form N_2 and CO_2 (Reaction 7), or with NO to form N_2 and CO (Reaction 8). The reaction of nitrile species with O_2 (Reaction 9) could result in the formation of NO and CO. While not indicated, the CO released in Reactions 8 and 9 envisioned to undergo further oxidation to CO_2.

The reaction sequence presented in Fig. 6 is consistent with the mechanistic arguments given previously by Li et al. [35], who proposed that the first step in the reduction of NO by CH_4 over Co-ferrierite is the reaction of gas-phase CH_4 with adsorbed NO_2, but differs in regard to the sequence of reactions leading to N_2 and CO_2. It is noted that the possibility of CN serving as a precursor to N_2 and CO_2 was suggested recently by Li et al. [38], based on studies conducted with Cu/ZrO_2 and by Hayes et al. [39] based on studies conducted with Cu-ZSM-5.

The proposed mechanism is attractive in that it explains not only the manner in which NO_2 initiates the reaction of CH_4, but also the pathway to CO_2 and N_2. This mechanism would also explain why NO facilitates the combustion of CH_4 by O_2 [28,30]. TPD experiments conducted in our laboratory have shown that Co-ZSM-5 will not adsorb O_2, whereas it will adsorb NO_2. If the product of the reaction of CH_4 with NO_2 is retained as an adsorbed species, then it is easy to see how NO_2 (derived from the oxidation of NO) could facilitate the oxidation of CH_4 by O_2.

4. Conclusions

Considerable insight into the nature of adsorption sites and the mechanisms by which NO decomposition and reduction occur over metal-exchanged ZSM-5 can be gained by combining information obtained from experimental and theoretical studies. The combined results of these studies support the view that NO decomposition over Cu-ZSM-5 requires both Cu^+ and $Cu^{2+}O^-$ sites. NO adsorbs on the first of these sites and then react with a second molecule of NO to produce N_2O and $Cu^{2+}O^-$. The latter species then reacts with either N_2O to form N_2 and $Cu^{2+}(O_2-)$. O_2 is produced by decomposition of $Cu^{2+}(O_2-)$. This process also restores the supply of Cu^+.

The reduction of NO over Co-ZSM-5 is greatly enhanced by oxidation of NO to NO_2, a species that remains strongly adsorbed even at elevated temperatures. The experimental evidence suggests that gas-phase CH_4 reacts with adsorbed NO_2 releasing water and forming CN. The CN groups then react with gas-phase NO_2 to form N_2 and CO_2, or with O_2 in a competing reaction to form NO and CO_2.

Acknowledgements

This work was supported by a grant from the Gas Research Institute.

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